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6. AUTHOR(S)
Daniel Rittschof, Donald G. Gerhart, Anthony S. Clare

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Duke University Marine Laboratory
135 Duke Marine Lab Road
Beaufort, NC 28516-9721

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000

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We focused our efforts on laboratory and field studies of easy-release and antifouling coatings and their additives. Goals were: 1.) understanding how the best coatings prevent barnacle fouling; and 2.) developing the ability to predict when, and to determine why, coatings fail. Leaching of additives from foul release coatings plays a significant role in prevention of larval settlement on all of the best antifouling and foul release coatings. Some additives are broad-spectrum toxicants, while others are toxic to specific kinds of larvae by altering their immediate environment. All effective coatings produced leachates toxic to barnacle larvae. Measuring additive levels in coatings and the rate of leaching from experimental coatings into water can be used to predict when coatings will fail. In collaboration with scientists at the University of New Hampshire, we showed the utility of experimental approaches in which coatings were designed to fail predictably over time. In addition to this work, we met our responsibilities in the area of patents and publications.

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FINAL REPORT

GRANT #: N00014-92-J-1516

PRINCIPAL INVESTIGATORS: Dr. Daniel Rittschof,
Dr. Donald G. Gerhart,
Dr. Anthony S. Clare

INSTITUTION: Duke University Marine Laboratory

GRANT TITLE: Nontoxic/Non-polluting Protection of Submerged Surfaces against Fouling

AWARD PERIOD: 1 January 1992 - 30 April 1995

OBJECTIVE: To investigate easy release and antifouling coatings and their additives through laboratory and field studies. The objectives were two-fold: 1) understanding how the best coatings prevent barnacle fouling; and 2) developing the ability to predict when, and determine why, coatings fail.

APPROACH: We developed, based upon type of fouling organisms, cluster analysis approaches to determine effectiveness of coatings.

ACCOMPLISHMENTS: The experiments showed that leaching additives play a significant role in prevention of larval settlement on all of the best antifouling and foul-release coatings. Some agents are broad-spectrum toxicants, while others may be toxic to specific kinds of larvae by altering their immediate environment. All effective coatings produced leachates toxic to barnacle larvae. Measuring additive levels in coatings and the rate of leaching from experimental coatings into water can be used to predict when coatings will fail due to additive depletion. In collaboration with scientists from the University of New Hampshire, we showed the utility of experimental approaches in which coatings were designed to fail predictably.

CONCLUSIONS: We showed that all effective coatings grow together with toxic coatings.

SIGNIFICANCE: We showed, in collaboration with scientists at the University of New Hampshire, the utility of experimental approaches in which coatings were designed to fail predictably.

PATENT INFORMATION:

(PATENTING & TECHNOLOGY TRANSFER--DUKE UNIVERSITY PROGRAM)

1. Costlow, J.D., Hooper, I.R., and Rittschof, D. Anti-fouling compound and method of use. U.S. Patent #4,788,302 awarded on November 29, 1988. (General subject area: antifouling agents from the octocorals Leptogorgia virgulata and Renilla reniformis). We are not actively pursuing this technology because it is less commercially feasible than our other related technologies.

2. Gerhart, D.J., Rittschof, D., and Hooper, I.R. Antifouling composition comprising lactone compounds, methods for protecting aquatic structures, and articles protected against fouling organisms. U.S. Patent # 5,248,221 awarded September 28, 1993. Intent to file foreign patents identified (PCT Application filed 13 October 1993). (General subject area: lactone analogs of natural antifoulants)

3. Gerhart, D.J., Rittschof, D., and Bonaventura, J. Antifouling coating comprising steroidal compounds and method for using same. U.S. Patent #5,252,630 awarded on October 12, 1993. (General subject area: steroidal toxins for fouling control)

4. Gerhart, D.J., Rittschof, D., Hooper, I.R., and Clare, A.S. Antifouling composition comprising furan compounds, methods for protecting aquatic structures, and articles protected against fouling organisms. U.S. Patent # 5,259,701 awarded November 9, 1993. Intent to file foreign patents identified (PCT Application filed 13 October 1993). (General subject area: furan analogs of natural antifoulants)

5. Gerhart, D.J., Rittschof, D., and Bonaventura, J. Antifouling coating and method for using same. U.S. Patent # 5,314,932 awarded May 24, 1994. [Duke File No. 00562 DIV.]

6. Gerhart, D.J. Antifouling coating comprising cyclohexane compounds and method for using same. Filed October 15, 1992 with the United States Patent and Trademark Office. In review by the USPTO. (General subject area: cyclohexane analogs of natural antifoulants)

ADDITIONAL RELATED INFORMATION - TRANSITION TO INDUSTRY: STATUS OF DUKE-DEVELOPED TECHNOLOGIES:

An option to license the furan, lactone, and cyclohexene analogs is currently held by Rohm & Haas Company. Industrial application is being examined by this corporation.

Licensees are being sought for the steroidal antifoulant molecules. Industrial application is complicated by the toxic nature of these substances. However, specific industries have indicated an interest.

Technologies identified in the Costlow et al. patent (U.S. patent #4,788,302) are not under license. Licensees are not being sought. Potential industrial application is unlikely at this time due to the limited availability of the natural compounds or extracts containing them, and the expense associated with synthesizing and purifying active compounds.

AWARD INFORMATION:

PUBLICATIONS AND ABSTRACTS:

1. Clare, A.S., D. Rittschof, D.G. Gerhart, I.R. Hooper and J. Bonaventura. (1998) Antisettlement and narcotic action of analogues of diterpene marine natural product antifoulants from octocorals. Biofouling (In press).

2. Rittschof, D. (1998) Fouling and natural product antifoulants, in M. Fingerman, R. Nagabhushanam, and M.-F. Thompson (eds.). Recent Advances in Marine Biotechnology. Oxford & IBH Publishing, New Delhi. (In press.)

3. Rittschof, D. and E.R. Holm. (1997) Antifouling and foul-release: A primer, pp. 497-512, in M. Fingerman, R. Nagabhushanam, and M.-F. Thompson (eds.). Recent Advances in Marine Biotechnology. Oxford & IBH Publishing, New Delhi.

4. Bryan, P.J., D. Rittschof, and J.B. McClintock. (1996) Bioactivity of echinoderm ethanolic body-wall extracts: An assessment of marine bacterial attachment and macroinvertebrate larval settlement. J. exp. Mar. Biol. Ecol. 196: 79-96.

5. Clare, A.S., D. Rittschof, R.R. Price, and D.J. Gerhart. (1995) Khellin, a natural product analogue with antifouling activity: Laboratory and field studies, pp. 573-580 in A. Bousher and R.G.J. Edyvean (eds.). Biodeterioration and Biodegradation. Institute of Chemical Engineers, Rugby, UK.

6. Clare, A.S., R.F. Thomas, and D. Rittschof. (1995) Evidence for the involvement of cyclic AMP in the pheromonal modulation of barnacle settlement. J. exp. Biol. 198: 655-664.

7. Sasikumar, N., A.S. Clare, D.J. Gerhart, D. Stover, and D. Rittschof. (1995) Comparative toxicities of selected compounds to nauplii of Balanus amphitrite amphitrite Darwin

and Artemia sp. Bull. Environ. Contam. Toxicol. 54: 289-296.

8. Vasishtha, N., D.C. Sundberg, and D. Rittschof. (1995) Evaluation of release rates and control of biofouling using monolithic coatings containing an isothiazolone. Biofouling 9: 1-16.

9. Clare, A.S., S.C. Ward, D. Rittschof, and K.M. Wilbur. (1994) Growth increments of the barnacle Balanus amphitrite amphitrite Darwin (Cirripedia). J. Crustacean Biol. 14(1): 27-35.

10. Maki, J., A.B. Yule, D. Rittschof, and R. Mitchell. (1994) The effect of bacterial films on the temporary adhesion and permanent fixation of cypris larvae, Balanus amphitrite Darwin. Biofouling 8: 121-131.

11. Price, R.R., M. Patchan, D. Rittschof, A.S. Clare, and J. Bonaventura. (1994) Performance enhancement of natural antifouling compounds and their analogs through microencapsulation and controlled release. In: Recent Developments in Biofouling Control, M.-F. Thompson, R. Nagabhushanam, R. Sarojini, and M. Fingerman (eds.), pp. 321-334. Oxford and IBH Publ. Co., New Delhi.

12. Rittschof, D., N. Sasikumar, D. Murlless, A.S. Clare, D.J. Gerhart, and J. Bonaventura. (1994) Mixture interactions of lactones, furans, and a commercial biocide: toxicity and antibarnacle settlement activity. In: Recent Developments in Biofouling Control, M.-F. Thompson, R. Nagabhushanam, R. Sarojini, and M. Fingerman (eds.), pp. 269-274. Oxford and IBH Publ. Co., New Delhi.